

HIGHLY ATTRITION-RESISTANT MOVING BED ZINC TITANATE SORBENT

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INTRODUCTION AND BACKGROUND

There is great optimism for the future of systems which generate electrical power from coal gasification product gases, and hot gas desulfurization (HGD) makes these systems more economically attractive. The present focus of E&A Associates' R&D program is on the development of a sulfur sorbent for one such Integrated Gasification Combined Cycle (IGCC) System, the one just installed by the Tampa Electric Company in Lakeland, Florida. HGD will be accomplished by moving bed technology developed by the General Electric Company. The qualification of sulfur sorbents to be used in the system is still in progress.

The author and his co-workers have been engaged in hot gas desulfurization research since 1991 (1-9). Work on zinc titanate sorbents began in 1992 with bench-scale evaluation of hand-made pellets. Both then and now, emphasis has been placed on obtaining high strength and durability, while maintaining good chemical reactivity. At the time this research started, other investigators had been able to obtain good reactivity, but attrition and decrepitation resistance was poor. The approach taken by the author to obtain good mechanical properties was to incorporate zinc titanate in a structural matrix of excess titanium dioxide. In addition, relatively coarse (2 micron) oxide powders were used as starting materials, and sintering or calcining was carried out at a high temperature (1000°C).

Using this approach, it was possible to obtain a crush strength that was 6 or more times higher than crush strengths obtained by prior zinc titanate investigators (5). High strength was achieved at the expense of sulfur capacity, a consequence of the relatively low zinc oxide content of 33.5 wt. pct. Another important characteristic of the sorbent was that the pore structure changed over the first several sulfidation-regeneration cycles. The chemical reactivity was poor during the first cycle but became progressively better as a network of fine pores developed. The change in pore structure was readily apparent when fresh and reacted materials were studied under a scanning electron microscope.

In the early stages of the program, there was interest in developing sorbents which could be used at temperatures above 600°C (1112°F) without excessive vaporization losses of zinc. A year was spent showing that doping of zinc titanate with third metal ions could provide this capability (6). The best dopant was found to be chromium. Currently, however, there is a need to extend the temperature capability down rather than up. The main reason is that valves and particle filters in HGD systems are not available to match the high temperature capabilities of sulfur sorbents.

The next step in the program was to try to produce sorbent pellets with good properties using established manufacturing methods (9). In this phase of the work, pellets were produced by an extrusion and rolling process in the pilot plant of United Catalysts, Inc. The transition from hand-made to pilot plant production of pellets proved to be more difficult than expected. Changes had to be made in raw materials, chemical composition, and calcining temperature before satisfactory properties were obtained.

Several other laboratories have been developing sorbents for the same application. Some of the details of our recent work, as well as those of the competing laboratories are proprietary, so it is not possible to review all of their similarities and differences. Generally there is much more information available on test data than on chemical composition and preparation methods.

All of the competing sorbents rely on zinc compounds as desulfurization agents. The General Electric Co. has been working for several years on a zinc titanate sorbent. The approach being taken to obtain high strength and durability is to add a few percent molybdenum oxide to the formulation. Currently, attempts are continuing to improve strength and to obtain good reactivity at temperatures as low as 350°C or 662° F (10).

TDA Research, Inc., is also developing a zinc titanate sorbent (11). The approach does not appear to be much different than that of the author. A high titania/zinc ratio is the mechanism of achieving good mechanical properties.

For both moving bed and other applications for sulfur sorbents, the Phillips Petroleum Co. has been conducting R & D for nearly twenty years. Phillips takes a traditional catalyst development approach in sulfur sorbent technology. Several ingredients are used in the formulation, each with a separate function in the material. The name given to Phillips recently developed set of sorbents is Z-Sorb" (12). This name is not mentioned in any of the patents, but a comparison of patents and publications (12-14) leads to the conclusion that Z-Sorb sorbents contain zinc oxide as the principal desulfurizing agent, silica and/or alumina as the structural matrix, and a third oxide as a so-called promoter. The latter, of which nickel oxide is an example, is supposed to enhance low temperature reactivity.

One other sorbent development project should be mentioned. Staff at the DOE Federal Energy Technology Center in Morgantown, WV, have been working for several years on zinc-based sorbents; the most recent formulation is called METC-10. Again one must examine both patent literature (15) and publications (16) to relate preparation procedures to properties. In the patent, it is stated that the principal ingredients are zinc oxide, titania as a diluent, high surface area silica gel as a support material, and a binder. Pilot plant testing by General Electric Co. has been done. However, operational problems made it difficult to judge the results.

CURRENT PROJECT OBJECTIVES

When the project started in May, 1997, the objectives were to produce 14,000 lb. of sorbent, verify that its properties (as measured in the laboratory) were satisfactory, and ship the material to the General Electric Co. for testing at its pilot plant in Schenectady, NY. Funding for GE's test

was to be provided by the U.S. Department of Energy. While the work was in progress, DOE decided to decommission the pilot plant and carry out all future scale-up testing in a slipstream at the Tampa Electric Plant. We therefore agreed to manufacture only a small quantity of material this year for additional DOE-sponsored laboratory testing.

INITIAL SORBENT PRODUCTION AND EVALUATION

The first step in making scale-up plans was to identify suppliers of raw materials who could meet the desired property specifications, delivery schedules, and costs. In prior work, oxide powders were purchased from Fisher Scientific and Johnson Matthey Co. as high purity chemicals. Obtaining a commercial supplier of zinc oxide was straightforward, but procurement of titania was difficult. Johnson Matthey's source priced its material at four times the price of pigment grade titania and needed five months lead time for production. Eventually another company agreed to make material to meet our specifications, even though it had not produced that grade of material before. The cost quoted was nearly the same as for pigment grade, which is made by several companies.

Since the new raw materials differed somewhat from those used previously, some 5 lb batches of sorbent were made in the pilot plant of United Catalysts, Inc., to adjust procedures to obtain the desired sorbent properties. These properties were then checked in the laboratories of United Catalysts, Southern Illinois University, and Research Triangle Institute (RTI). The pellets were 3.5 to 5.0 mm dia.

A total of 9 pilot plant trials were made under a variety of conditions during the period from May to August, 1996. In the last of the 9 preparations, a judgement was made on the processing parameters which should have given the best combination of properties, which was named formulation ICCI-2B. Both its physical properties and performance in a fixed bed laboratory test were similar to those obtained earlier with hand-made pellets and different raw materials (5,9). X-ray diffraction measurements showed clear peaks only for Zn_2TiO_4 and TiO_2 (rutile).

SPECIFICATION CHANGES

In August, 1996, two important events occurred. First, planned tests at GE's moving bed test facility were postponed as questions were raised about the affordability of future tests and the value of results of earlier tests. One of the concerns was that the Lurgi gasifier at GE's test facility deposits tar on the sorbent, a condition that will not occur at the Tampa Electric Plant, where a Texaco gasifier is used. Testing of our ICCI sorbent was postponed because of this issue.

The second event was that sorbent developers were asked to show that their sorbents had properties that are compatible with expected Tampa Electric operating conditions. More specifically, both the sulfidation and regeneration temperatures are expected to be about 900°F or 482°C. This change is unfortunate because the sorbents were developed to work well at higher temperatures, and quick-response sorbent modifications could do more harm than good. The limits on regeneration gas composition are 3 to 7% O_2 in N_2 , values that were locked in when

there were concerns about controlling the temperature rise from the strongly exothermic regeneration reaction.

Since the exit gas from the regeneration gas goes to a sulfuric acid plant for byproduct sulfur recovery, the SO₂ content of the gas must be allowed to build up to a concentration of 10% at steady state. This requirement means that sorbents must regenerate well in the presence of 10% residual SO₂. The question this requirement raises is whether or not zinc sulfate formation in the sorbents will have an adverse effect on performance.

As a first step in addressing these issues, RTI was asked by DOE to carry out a series of tests on the ICCI-2B sorbent. Only a small amount of testing was completed before a budget problem developed and the tests were stopped. The most important result reported was that the regeneration reaction was self-sustaining at 900°F, if the gas flow space velocity was reduced from 2,000 to 1,000 hr⁻¹. The gas composition was 5% O₂ in N₂. The reduced space velocity meant that there was less convective cooling of the sorbent, allowing the temperature of the sorbent to increase enough to sustain the reaction.

PRODUCTION TRIALS IN UCI'S MANUFACTURING PLANT

To make 14,000 lb of material, as originally called for in the contract, procedures had to be developed to meet sorbent property requirements with large scale manufacturing equipment. Initial attempts to do this were unsuccessful. The extrusion dies overheated because of high friction associated with the relatively coarse oxide powders in the formulation. The starch binder tended to burn out, and the paste feeding the extruder disintegrated before pellets formed. The problem was eventually solved by thinning the dies and abandoning the use of starch as a binder. After several trials, success was achieved with a substitute binder. A small lot of this material, designated ICCI-2C, was produced. A portion was sent to GE and the remainder was given to Southern Illinois University for evaluation.

EVALUATION OF ICCI-2C SORBENT

The physical properties of ICCI-2C obtained at four different laboratories are listed in Table 1.

Table 1. Physical Properties of ICCI-2C Prepared in Manufacturing Plant

Property	UCI Value	GE Value	RTI Value	SIUC Value
Crush Strength (lb)	24.8	25.6 for 4-5mm Pellets 19.2 for 3-4mm Pellets	30.9	32.5
ASTM Attrition Loss (%)	0.5	2.2	2.1	--
Bulk Density (lb/ft ³)	97.2	--	--	--
Pore Volume (cm ³ /g)	0.19	--	0.17	--
Mean Pore Dia. (Å)	4011	--	4994	--
BET Surface Area (m ² /g)	1.98	--	0.96	--

Note that there is a disturbingly large difference in crush strength, attrition loss, and BET surface area values between laboratories, which is not understood. However, if one compares the properties of ICCI-2C (manufacturing plant material) with those of ICCI-2B (pilot plant material), the variations are small, when one considers that both the equipment and binder used were different. Even though the physical properties of ICCI-2C were good, it was decided to carry out reactivity experiments at SIUC before shipping material to GE for evaluation. GE's testing was supposed to judge the material's acceptability for the scale-up test in its facility in Schenectady, NY. GE was also asked by DOE to determine whether or not there would be problems with a follow-on test at Tampa Electric. More specifically, GE was to study sensitivity to residual SO_2 in the regeneration gas and initiation of the regeneration reaction at 900°F .

A series of thermogravimetric analysis (TGA) experiments carried out at SIUC proved to be particularly interesting and informative. Fig. 1(a) shows results of an experiment in which the reaction temperature was 610°C (1112°F). The gas composition for sulfidation was 6.3% H_2S , 56.3% H_2 , 35.7% He , and 1.8% H_2O . For regeneration, the base composition was 5% O_2 and 95% N_2 . In the first cycle, no SO_2 was added to the gas during regeneration, and the results gave expected behavior. In the second cycle, 10% SO_2 was added during regeneration. It can be seen that the regeneration reaction started as before, but after approximately 15 minutes, weight loss evolved into weight gain. This weight gain is attributed to zinc sulfate formation, which is highly undesirable. In TGA tests, convective cooling from the gas is believed to keep the temperature of the specimen relatively constant. Therefore the temperature of the specimen cannot rise enough to reach a temperature at which zinc sulfate is unstable.

This effect was studied further by carrying out the regeneration reaction at higher temperatures. In Fig. 1(b), the regeneration part of a TGA experiment is shown for a regeneration temperature of 732°C (1350°F). The regeneration reaction continued to completion, but holding the specimen for a longer time resulted in the onset of sulfate formation. It is surprising that regeneration and sulfate formation occurred in two distinct stages. This behavior can be used to advantage, however, in that careful control of regeneration time can result in complete regeneration without allowing the formation of sulfate. Similar data for a regeneration temperature of 815°C (1499°F) are shown in Fig. 1(c). Note that complete regeneration occurred, and no sulfate formation occurred. A thermodynamic calculation showed that zinc sulfate is unstable at 815°C , so there was consistency between theory and experiment.

SIUC also performed fixed bed experiments on crushed pellets of the ICCI-2C sorbent. In a six-cycle test, regeneration was carried with and without 1% residual SO_2 in the regeneration gas. The sulfidation temperature was 482°C (900°F). The performance of the sorbent was essentially the same as its precursors. As activation proceeded, breakthrough occurred at a progressively higher percentage of theoretical bed capacity. During the 1st cycle, it was 15%; it was 33% for the third, 51% for the fifth, and 76% for the sixth cycle. No adverse effect of 1% residual SO_2 was detected. The temperature rise in the bed was monitored carefully during the fifth regeneration cycle. The temperature increased from 658°C to a maximum of 716°C at a reaction time of 30 minutes. The temperature rise in the bed of 58°C or 104°F undoubtedly was helpful in suppressing sulfate formation.

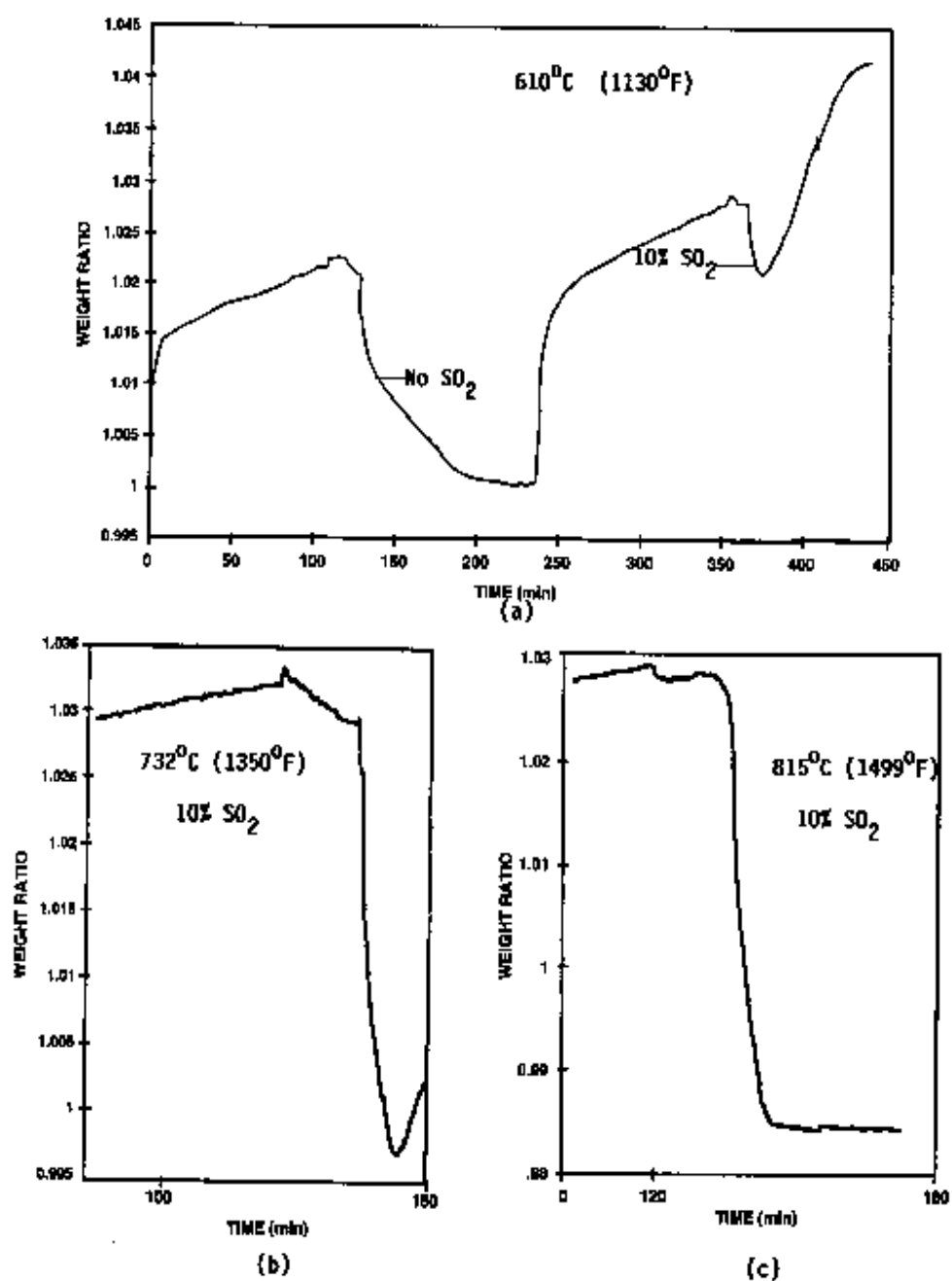


Figure 1. TGA Results on Effect of Adding 10% SO₂ to Regeneration Gas.

Additional experiments were done in the fixed bed apparatus at SIUC to study possibilities for lowering the initiation temperature for regeneration. Success was achieved in obtaining a self-sustaining reaction down to an initial temperature of 556⁰C (1033⁰F). At lower temperatures, the reaction started and stopped after a few minutes. Increasing the O₂ concentration from 5 to 7.5% did not have a noticeable effect.

An idea that was pursued briefly at SIUC was to try to generate more heat in the sorbent bed through a catalytic reaction. More specifically, a few percent carbon monoxide and extra oxygen was added to the regeneration gas to oxidize the carbon monoxide catalytically to carbon dioxide. The experiments were unsuccessful, probably because the reaction occurred in the lower part of the reaction tube rather than in the sorbent bed. The idea might still have merit if a better method were devised to introduce the combustion gas.

Finally, in the series of experiments at SIUC on the ICCI-2C sorbent, six sulfidation-regeneration cycles were carried out in the fixed bed apparatus to study cracking and decrepitation resistance. Sulfidation and regeneration were carried out at 482 and 610°C, respectively. No SO₂ was added to the regeneration gas. Upon completion of the test, the pellets were studied under a scanning electron microscope (SEM). None of the pellets had cracked; Fig. 2 shows an SEM picture of three of the pellets. Crush strength measurements were made on 20 of the pellets. The average strength was 30.5 lb, compared to 32.5 lb for the fresh material. Since the standard deviations of the data were about 6 lb, the difference in values of the fresh and reacted materials may or may not be real.

Since the results summarized above for the ICCI-2C sorbent were generally positive, a sample was shipped to GE for evaluation. Preliminary work there consisted of mechanical property (see Table 1) and TGA measurements. Then a 13 cycle fixed bed test was conducted, with variations made in test conditions. Sulfidation was carried out at 900°F, 5 atm pressure, 1% H₂S in the gas, and a space velocity of 2000 hr⁻¹. For regeneration, the conditions were an initial temperature of 900°F, 1.5 atm pressure, 5% O₂, and a space velocity of 700 hr⁻¹. After it became clear that the reaction was proceeding, the furnace temperature was raised to 1100°F. This step was taken to simulate or approximate the temperature increase that would occur when pellets are used in GE's moving bed system. SO₂ was added to the regeneration gas beginning with the 7th cycle. The amount added was 1% for cycles 7-10, and 10% for cycles 11-13.



Figure 2. Scanning Electron Micrograph of ICCI-2C Pellets After Six Sulfidation-Regeneration Cycles.

Sulfidation breakthrough curves for the GE test are plotted in Fig. 3, and breakthrough times obtained from the data are plotted in Fig. 4.

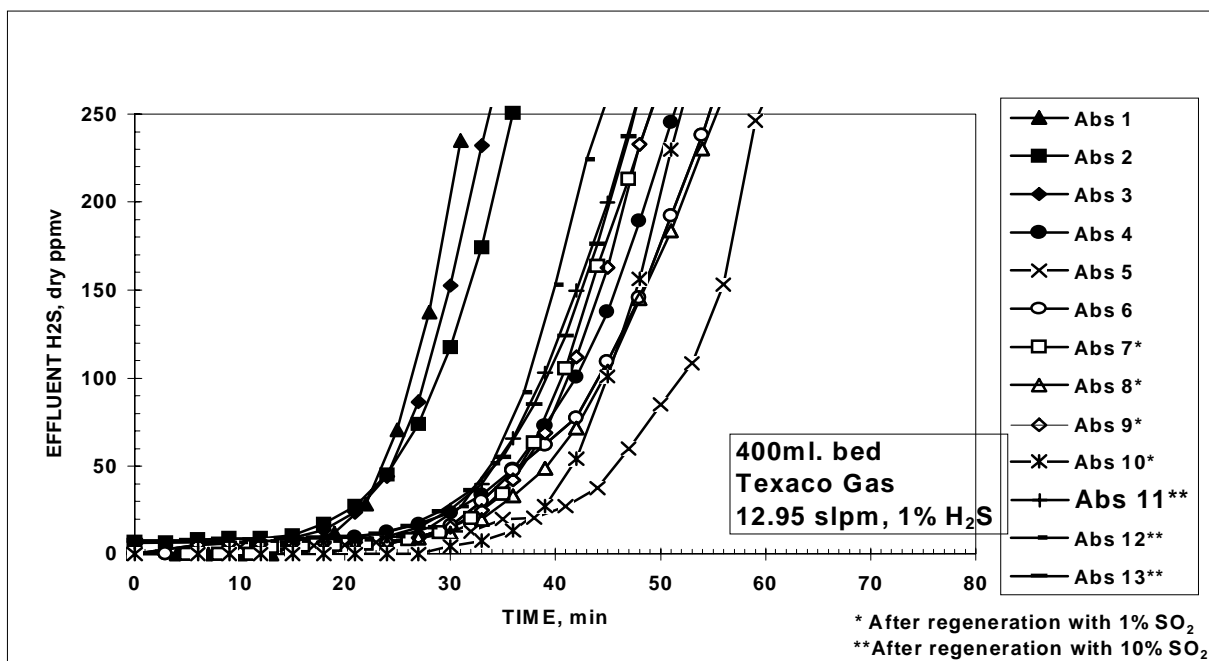


Figure 3. Sulfidation Breakthrough Data for Sorbent ICCI-2C Tested by General Electric Company.

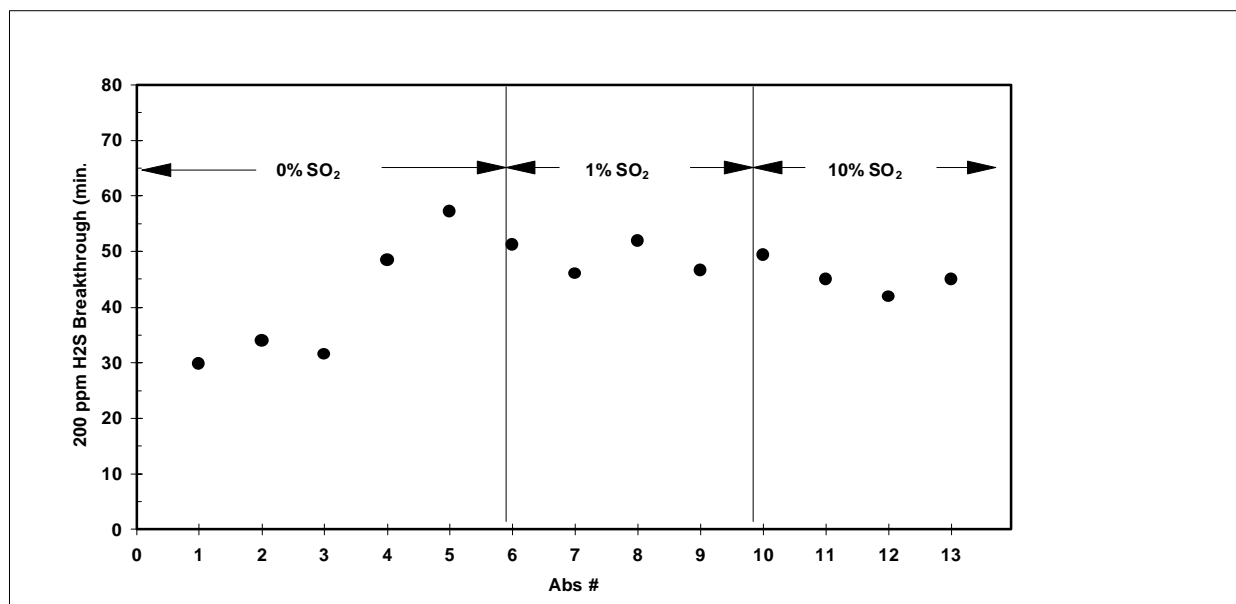


Figure 4. Breakthrough Times Taken From the Data Plotted in Figure 3.

Premature breakthrough occurred during cycles 1-3 as activation of the sorbent proceeded. Comparing data in Fig. 5 for cycles 4-6 versus 7-10, only a slight loss in breakthrough time and bed efficiency occurred when 1% SO₂ was added. For cycles 11-13, the loss was again small when the SO₂ concentration was increased from 1 to 10%. The peak temperature in the bed during regeneration was generally 1350°F.

After the test, checks were made on attrition resistance and sulfate content of the pellets. After the 13th regeneration, the ASTM attrition resistance of pellets located near the gas inlet was 1.89%. Near the gas outlet it was 2.09%. Remembering that GE's value for the fresh sorbent was 2.16%, the degradation occurring during the test was relatively small. The requirement is 5% or less.

The residual amount of total sulfur in pellets located near the gas inlet after the 13th regeneration was 0.66%. Of that amount, 0.16% was sulfatic. The corresponding values for pellets located near the gas exit were 0.26 and 0.04%, respectively. Total loading during sulfidation was approximately 7% sulfur as zinc sulfide. These data indicate that buildup of undesirable sulfate during the test was not a serious problem. Overall, the results of the tests carried out by General Electric were encouraging.

TWENTY FIVE CYCLE TEST

Late in 1996, the U.S. Department of Energy (DOE) issued a plan to sponsor a new qualification test for sorbent developers who wished to have their products used at the Tampa Electric plant. One or more qualified sorbents would be evaluated at the plant after system shakedown tests were completed on Phillips' Z-Sorb material already delivered. As a part of this plan, E&A Associates was encouraged to supply ICCI-2C material for testing at the Research Triangle Institute. The inventory of material was too small to supply the amount RTI required, so a new batch was made. The resulting physical properties were somewhat different than for the first batch, so some of the material was recalcined at a slightly higher temperature to try to duplicate properties. The first sample was designated ICCI-2CL, and the second was designated ICCI-2CH. The L and H in the designations stand for low and high calcining temperatures. Both samples were shipped to RTI. The procedure to be followed was to conduct scoping or preliminary tests on both samples, then select one of the two for the 25 cycle qualification test. When TGA measurements were made, it was decided that the reactivity of the ICCI-2CH sample was too low to perform well in a fixed bed test under the current guidelines. Therefore, all of the results discussed below are for the ICCI-2CL sample. The results are summarized from a more detailed report prepared by RTI (17).

The apparatus for the tests consisted of an electrically heated quartz tube with equal gas pressures on the inside and outside. The 2 in. ID tube was filled with sorbent to a depth of 6 in. These dimensions corresponded to a sorbent mass of 0.93 lb. The reacting gas was taken from cylinders, with flow rates measured with mass flow controllers. A Varian 3300 gas chromatograph was used to measure the concentrations of sulfur-bearing gases exiting the bed.

The main purpose of the scoping tests was to determine an appropriate set of test conditions for successful regeneration. Before starting both the scoping and the 25 cycle qualification tests, 3 activation cycles were carried out. They consisted of sulfiding for a period of 125 minutes,

regardless of the H_2S level in the effluent. Meeting the objectives of the scoping tests took a considerable amount of effort. The sulfiding step proceeded without difficulty at 900°F . When the regeneration reaction was tried at the same temperature, initiation was no problem when the space velocity of the gas was kept low to reduce convective cooling of the pellets. However, the reaction did not continue to completion, and the temperature rise in the bed was only about 50°F . Next a procedure similar to that used in GE's test was tried. Regeneration was initiated at a temperature in the range of 900 to 1000°F . After a significant temperature rise and SO_2 evolution were observed, the furnace temperature was raised to complete the reaction. With this procedure, there was a problem with sulfate formation in the sorbent, due probably to the relatively slow increase in temperature to a level at which zinc sulfate is unstable. This problem was not observed in GE's test. There are two possible reasons. One is that GE's sample was activated more completely at the time the observations were made. The other is that heat loss characteristics in GE's apparatus are different than in the apparatus at RTI. It is important to point out that the thermal characteristics in a moving bed would be different than in either fixed bed apparatus.

Success was eventually achieved at RTI by starting the regeneration reaction at 1050°F and not adjusting the furnace temperature. For the first few cycles, an oxygen concentration of 7% was used without difficulty. With additional cycling, the bed overheated, as shown in Fig. 5. The peak

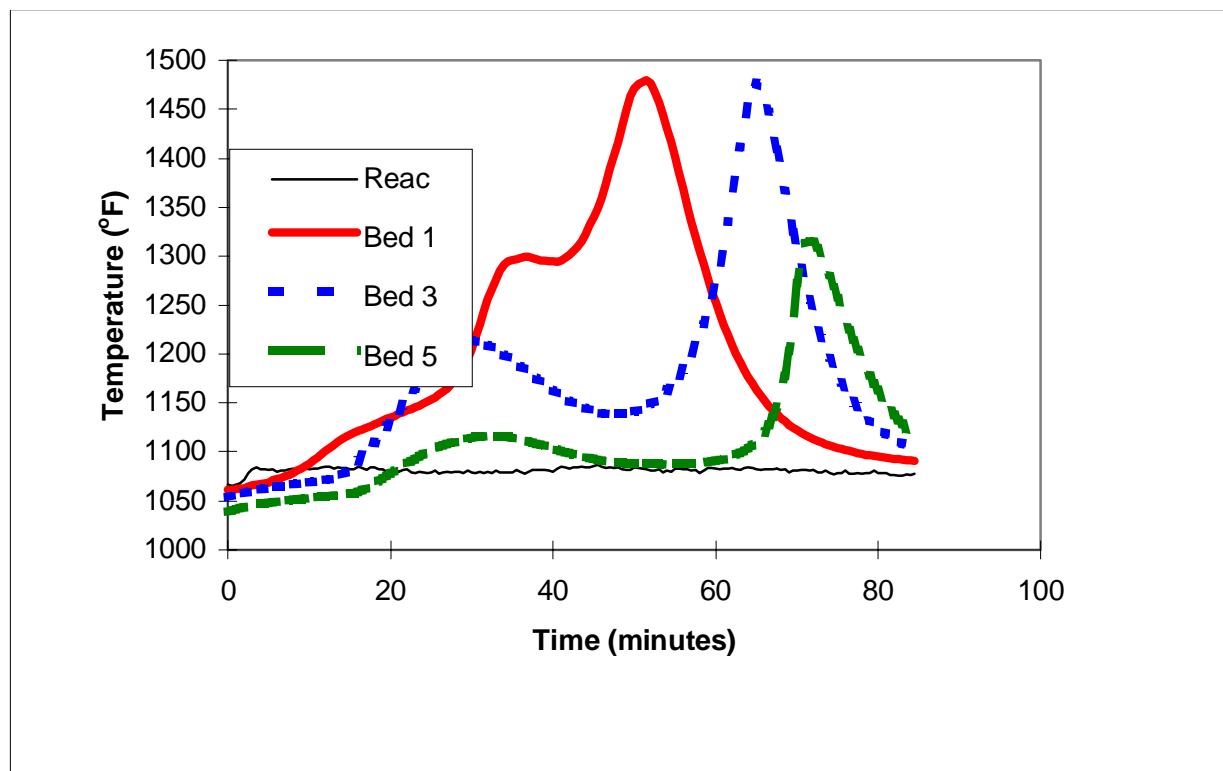


Figure 5. Overheating of Bed During Scoping Test with 7% O_2 in Regeneration Gas.

temperature exceeded 1450°F, which cannot be accommodated at the Tampa Electric plant and could damage the sorbent. The adjustment made to the test procedure to solve this problem was to lower the oxygen concentration from 7 to 3.5% after initiation of the regeneration reaction.

A fresh sample was loaded in the reactor for the 25 cycle test. A summary of test conditions is given in Table 2. Note that the amount of SO₂ added to the regeneration gas was increased sequentially from 1.5 to 6%. Since up to 4% evolved from the material, the SO₂ level reached a maximum of 10% during the tests. After the third cycle, it was determined that the oxygen concentration could be maintained at a constant value of 5% instead of changing it during the test. The reason is that additional activation of the sorbent occurred during the early stages of testing.

Table 2. Twenty Five Cycle Test Conditions

Reaction	Initial Temp. (° F)	Pressure (PSIG)	Space Velocity (h⁻¹)	Gas Composition (%)
Sulfidation	900	280	2000	5.9 N ₂ , 18.1 H ₂ O, 12.2 CO ₂ , 35.8 CO, 26.8 H ₂ , 1.2 H ₂ S
Regeneration (cycle 1)	1050	88	1000-2000	3.5-7 O ₂ , 1.5 SO ₂ Bal. N ₂
Regeneration (cycle 2)	1050	88	1000-2000	3.5-7 O ₂ , 3.5 SO ₂ Bal. N ₂
Regeneration (cycle 3)	1050	88	1000-2000	3.5-7 O ₂ , 6 SO ₂ Bal. N ₂
Regeneration (cycle 4-24)	1050	88	1000	5 O ₂ , 6 SO ₂ Bal. N ₂

The breakthrough behavior of H₂S during the test is described in Fig. 6. The activation cycles are denoted as A, B, and C. On the left side of the figure, the first 30 minutes are shown as "reductive regeneration". During this period, the sorbent was held under reducing conditions to decomposed retained zinc sulfate from the previous regeneration step. Prebreakthrough concentrations of H₂S were less than 10 ppmv during the first half of the test and increased gradually to about 30 ppmv at the conclusion. The behavior at longer reaction times can best be analyzed with the aid of Fig. 7. Here the H₂S levels in the effluent at a sulfidation time of 120 minutes are plotted. The low values for activation cycle C and cycle 1 are attributed to early difficulty in optimizing the regeneration procedure. Otherwise most of the values are in the vicinity of 100 ppmv. Mass balance calculations from the breakthrough curves were carried out to determine sulfur capacity of the sorbent as a function of cycle number. The results are plotted in Fig. 8. Sulfur loading of 20.7 grams corresponds to the specification of 6.7 lb/ft³ for the Tampa Electric system, so the requirement was met. The breakthrough data for the 25th sulfidation (not shown in the figure) gave a sulfur loading of 9.12 wt%, which corresponds to 7.79 lb/ft³. It is clear from these results that the presence of residual SO₂ had no significant adverse effect on sorbent performance.

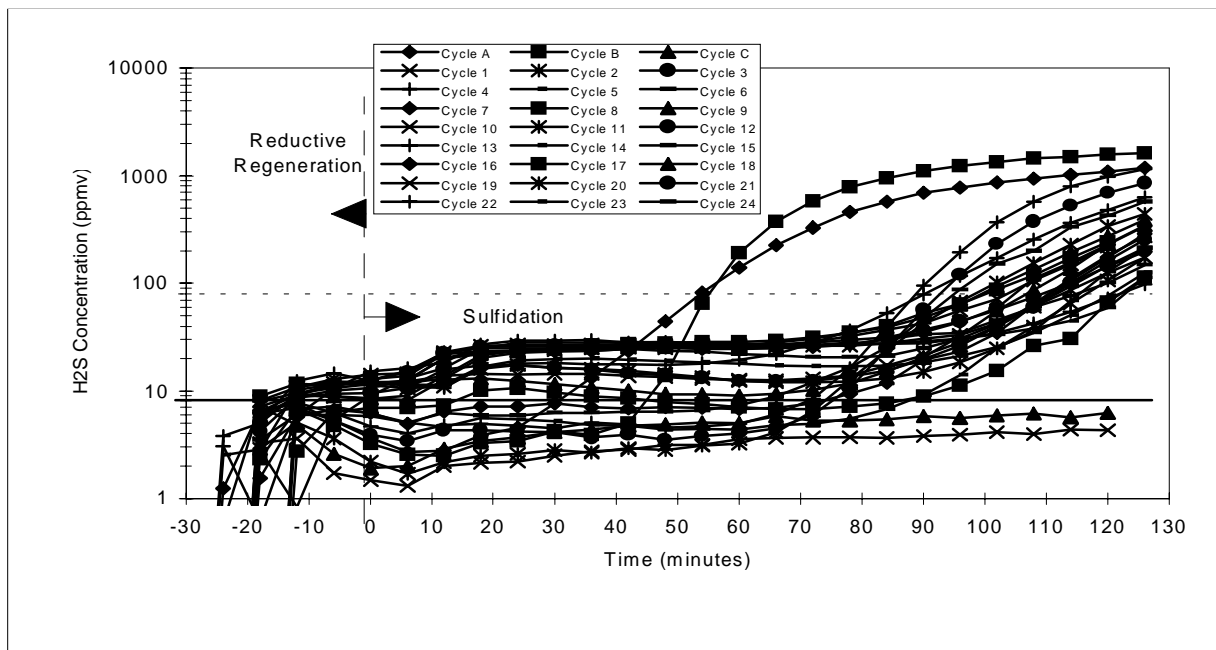


Figure 6. H₂S Breakthrough Behavior During 25-Cycle Test.

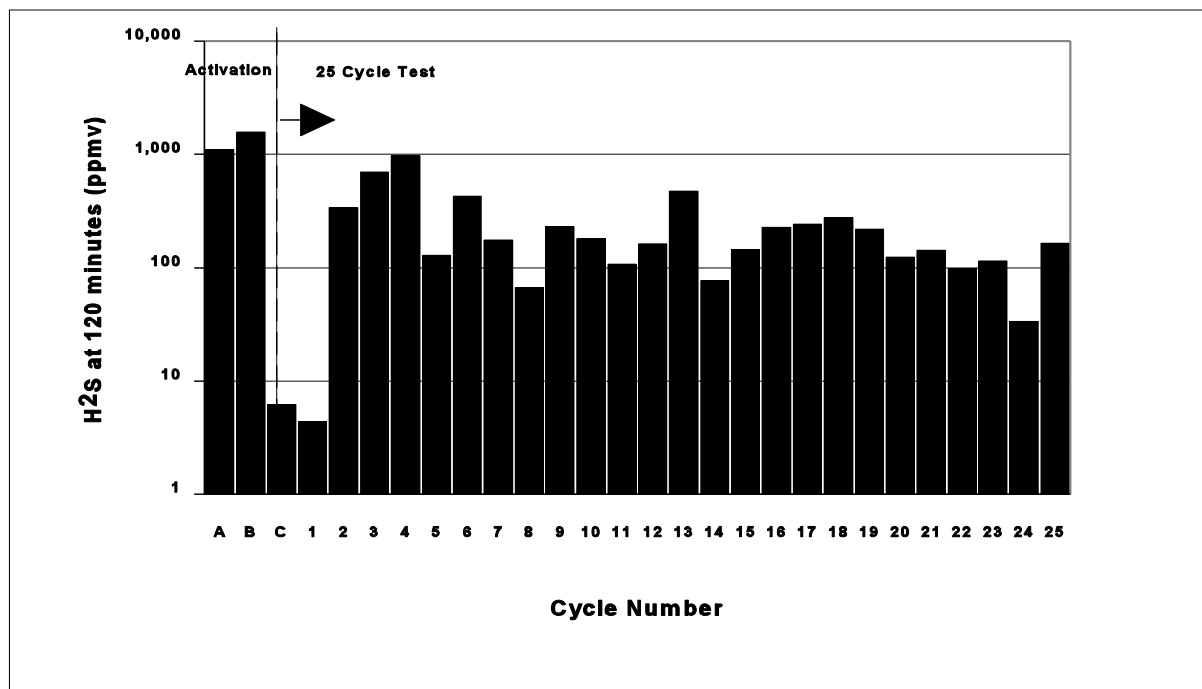


Figure 7. Envelope of H₂S Concentrations After 120 Minutes During 25-Cycle Test.

Examples of temperature rise and SO₂ evolution data are given in Figs. 9 and 10 for cycle 24. The three curves in Fig. 9 are for three different bed positions. It is believed that maintaining temperature in the range of 1150 to 1400°F during most of the regeneration time is best for minimizing sulfate formation without exceeding system high temperature limitations. The results on temperature rise meet this objective. In Fig. 10, SO₂ evolution can be seen to be very fast, reaching a level of 2 1/2% evolved plus 6% added in just 10 minutes. At approximately 110 minutes of reaction time, the SO₂ evolution proceeds toward completion, and oxygen begins to leak through the bed.

Physical and chemical properties of the fresh and reacted material are listed in Table 3. The second set of data corresponds to a sample removed from the reactor after the 24th regeneration. The remaining material was sulfided again, giving the properties listed in the last column. When one compares properties of the fresh and reacted samples, it can be seen that BET surface area and pellet density increase, while the pore volume, median pore diameter, and porosity decrease during the test. The same observations were made in earlier tests on ICCI sorbents. There were some losses in crush strength and attrition resistance, but the requirement that attrition loss below 5% for the reacted material was met. Note that there was 1.2% sulfate retained after the 24th regeneration. While this amount is not trivial, it did not have a serious effect on sorbent performance.

Another task in postmortem analysis was to compare TGA reactivities of a fresh sample with that of a sample after testing. The reactivity of the sample after testing was comparable to, but a little lower than that of the fresh sample. When all of the test results are considered, there are no trends which would suggest that the sorbent would degrade quickly over another 25 or more cycles.

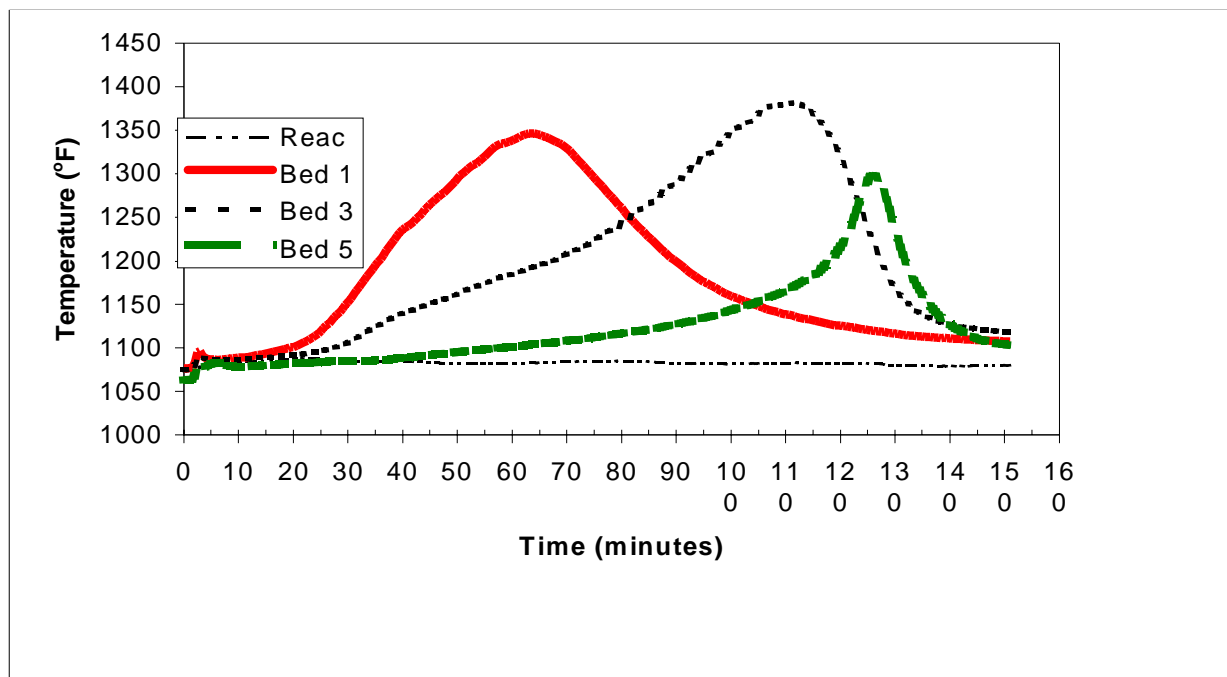
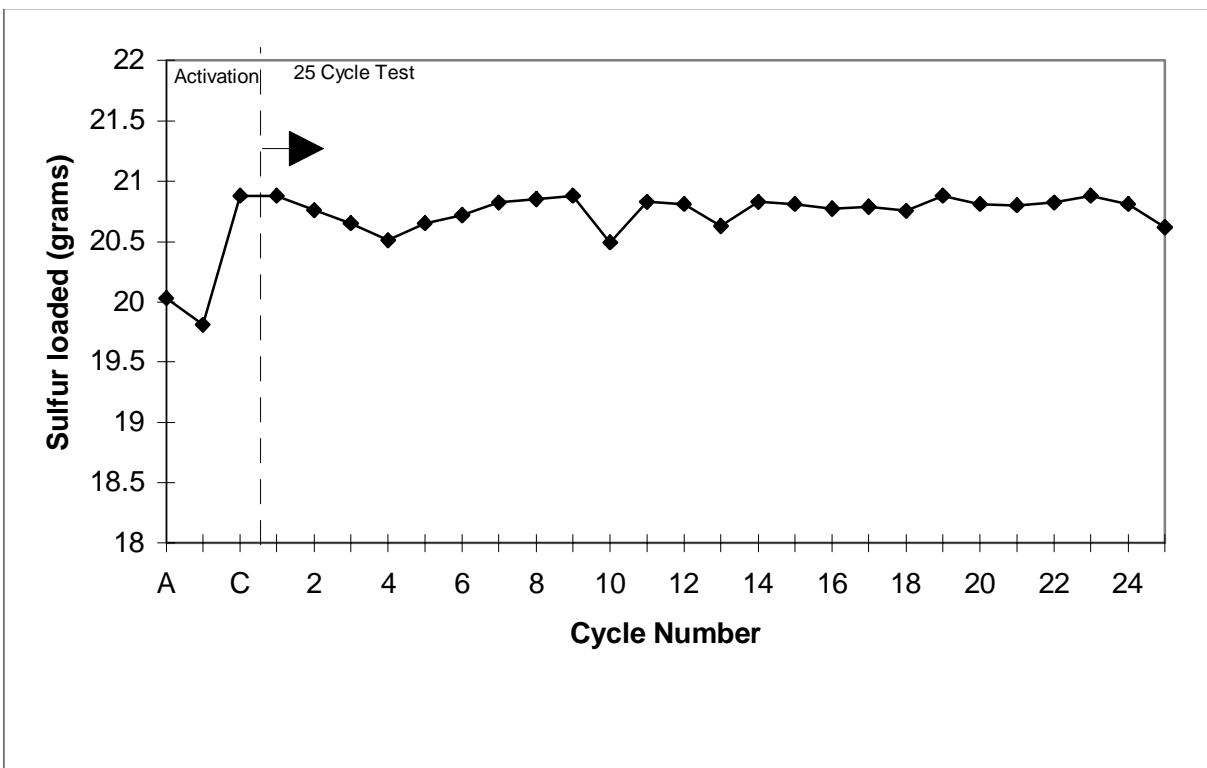


Figure 8. Sulfur Loading Data for 25-Cycle Test.

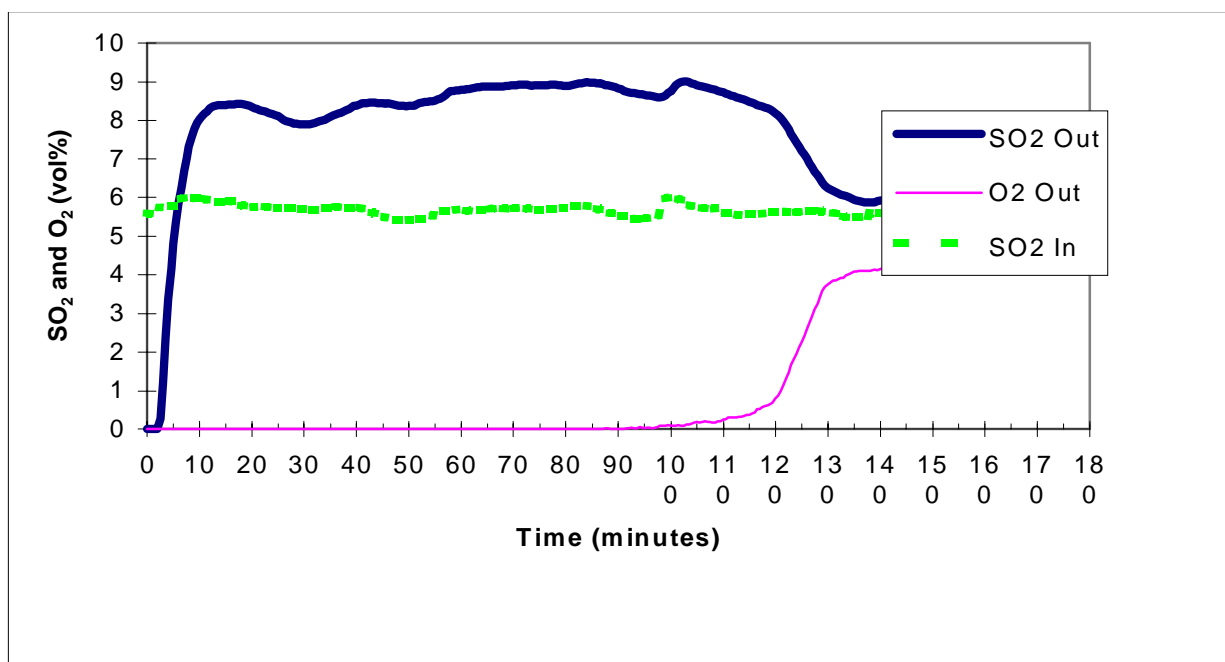


Figure 9. Temperature Rise of Bed During 24th Regeneration.

Table 3. Physical and Chemical Properties of Fresh and Reacted ICCI-2CL Sorbent

Property	Fresh	After 24th regeneration	After 25th sulfidation
BET Surface Area (m ² /g)	1.86	4.31	4.59
Mercury Pore Volume (cc/g)	.190	.118	.110
Median Pore Diameter (Å)	3312	2508	2854
Porosity (%)	45.9	32.07	29.15
Pellet Density (g/cc)	2.41	2.71	2.64
ASTM Attrition (wt%)	1.03	4.38	4.94
Crush Strength (lb/pellet)	20.44	13.3	15.2
Total Sulfur (wt.%)	0.37	3.76	9.12
Sulfate Sulfur (wt%) ^a	0.04	1.2	0.08

^aAnalyzed by Commercial Testing and Engineering Company.

Figure 10. SO₂ Evolution During 24th Regeneration.

CONCLUSIONS

The ICCI-2C sorbent meets specifications for the Tampa Electric plant, subject to the provisions that a 3 cycle activation procedure is used and that regeneration be initiated at 1050°F.

Temperature rise behavior during regeneration is of critical importance. It is not known how well lab tests simulate moving bed conditions; operating data from the plant are needed to shed light on this subject.

FUTURE ACTIVITIES

A decision is pending on whether or not the ICCI-2C sorbent will be tested at the Tampa Electric plant. While this possibility is being considered, the same sorbent formulation is being prepared on a small scale by spray drying to determine the feasibility of its possible use in transport reactor applications. Finally, a proposal has been written for the development of a new sorbent with better reactivity at temperatures down to 600°F. It is not a zinc titanate.

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DISCLAIMER STATEMENTS

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